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RESEARCH MEMORANDUM

OXIDATION-RESISTANCE MECHANISM AND OTHER PROPERTIES OF MOLYBDENUM DISILICIDE

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NATIONAL ADVISORY COMMITTEE
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SUMMARY

An experimental investigation was conducted to determine the oxidation-resistance mechanism, the melting characteristics, the electric resistivity, and the modulus of elasticity of molybdenum disilicide.

Molybdenum disilicide $MoSi_2$ bodies are protected from oxidation at high temperatures by the formation of a protective siliceous coating in which α-cristobalite has been identified as the sole or principal constituent. In powdered form, $MoSi_2$ is not inherently resistant to oxidation and burns in air at comparatively low temperatures. Molybdenum disilicide decomposed at the melting point with the loss of appreciable silicon. This phenomenon has so far prevented casting of satisfactory ingots. Decomposition below the melting point was indicated.

The electric resistivity of $MoSi_2$ at room temperature varies from 23 to 27 microhm-centimeters depending on the method of fabrication. The conductivity was found to be metallic in nature and to decrease with increasing temperatures to 2000° F.

The room-temperature modulus of elasticity as determined by a dynamic method was 59×10^6 pounds per square inch. Poor damping characteristics are indicated for the material at room temperature.

INTRODUCTION

The outstanding oxidation resistance of molybdenum disilicide $MoSi_2$ at high temperatures, as previously reported (references 1 and 2) and as summarized in table I, places it among the most resistant of materials in the temperature range from 2000° to 2850° F. Resistance to oxidation is one of the most important characteristics of material for turbine blades or for other high-temperature uses; the mechanism by which $MoSi_2$ resists oxidation is therefore of considerable interest. This interest is not confined to solid bodies of the material because work on

the protection of molybdenum at high temperatures has shown that silicon-containing coatings, which appear to derive their oxidation resistance from the presence of $MoSi_2$, offer considerable promise in the solution of this important protection problem (reference 3). A program was therefore initiated at the NACA Lewis laboratory to determine the mechanism by which $MoSi_2$ resists oxidation. The oxidation of the material in powdered form was also considered as having an important bearing on sintering and fabricating problems.

Because of the promising high-temperature strength and other properties of $MoSi_2$, as described in references 1 and 2, the possibility of forming the material by casting appeared well worth investigating. The decomposition of $MoSi_2$ at the melting point was studied in relation to its effects on casting properties and its possible relation to problems encountered in sintering at high temperature.

The specific electric resistivity of two forms of the material was also determined at temperatures up to 2000° F. From the practical standpoint, it was believed that these data could be used as a basis with which to compare the resistivities of other forms of the material of different degrees of purity. These resistivities would also furnish information on the metallic nature of $MoSi_2$ and related matters of theoretical interest. The modulus of elasticity for the material at room temperature was also determined.

The specimens used in this investigation were prepared at the laboratory in conjunction with a concurrent investigation of the strength and fabrication of molybdenum disilicide.

APPARATUS AND PROCEDURE

Oxidation-Resistance Mechanism

Oxidation of powdered $MoSi_2$. - The method of preparation of the powders is that described in reference 1 and consists in forming $MoSi_2$ by direct combination of the elements and grinding this raw material for 96 hours in water. The product is then purified by leaching with acids and caustic and dried in vacuum. The particle-size analysis as determined by microscopic methods was:

6 microns or less	100 percent of particles
1 micron or less	98 percent of particles

The ignition temperature of the powder was determined by heating samples of the powder in small crucibles in a laboratory furnace at a constant rate equivalent to 500° F in 20 minutes. One set of 3.0-gram samples and one set of 20-gram samples were tested seperately.

As it appeared reasonable to attribute at least the greater portion of the weight gain of $MoSi_2$ powder in clean dry air to oxidation, the oxidation rate of the powder was approximated by measuring the gain in weight of the powder at several intervals of time.

Weight-increase determinations for undisturbed powders standing in still air were made by weighing samples retained in weighing vials for set intervals. The samples were:

(1) Freshly prepared powder evaluated at room temperature. The first weighing was made 5 minutes after breaking the vacuum at the end of the drying period. The sample was retained in the balance case with a dehydrator between weighings.

(2) Powder evaluated at 212° F after exposure to air at room temperature for several weeks. The specimen was maintained at temperature in an oven during the test.

Protective surface coating. - The coating on oxidized $MoSi_2$ is so thin as to remain an unresolvable line in cross section under a high magnification; X-ray techniques of identification were therefore employed. The apparatus used was a North American Philips, Geiger counter, X-ray diffraction unit. In this equipment, a beam of X-rays is focused on the surface of the specimen and the intensity of the diffracted beam is measured by a Geiger counter moving along a quadrant in front of the specimen. The counter impulses are scaled and recorded on a self-balancing potentiometer recorder to form patterns as shown in figure 1. The Geiger counter moves at the rate of 0.5 degree per minute; angles can therefore be measured with considerable accuracy, and as the specimen is rotated at one-half the angular speed of the Geiger counter, the angle measured is 2θ in the Bragg equation. Intensity ratios (I/I_1) were obtained by direct measurement of the heights of the peaks above the background.

Melting and Casting

Melting operations were carried out in the bell-jar-type vacuum induction furnace shown in figure 2. In this equipment, the mold is fastened directly to the housing which holds the induction coil and the crucible. A tilting arrangement thru a vacuum seal makes it possible to revolve the whole unit into the pouring position. Because the charges used would not heat by induction, the crucible was surrounded by a closely wound coil of tungsten wire that served as a heater block. The crucibles were stabilized zirconia with perforated tungsten lids. Temperatures were determined with an optical pyrometer by sighting through a hole in the crucible lid. As the only view of the melt was thru the lid and as considerable fumes accompany melting, temperatures

of the molten $MoSi_2$ could not be determined with accuracy. The charges were held under a 5-micron vacuum for 1/2 hour, after which time argon was introduced until a positive pressure of 1 inch of mercury had been attained and heating started. Both solid copper and rammed zirconia molds were used.

The charge consisted of 100 grams of commercially available high-purity $MoSi_2$ similar to that described in reference 2. In order to prevent the $MoSi_2$, which was furnished as a 100-mesh powder, from being blown out of the crucible during evacuation, it was necessary to compact it. Pressing the powder at 40,000 pounds by the hydropress method gave a compact which, even though quite fragile, would withstand evacuation.

Electric Resistivity Measurements

Measurements on two specimens of slightly different impurity content were made; one was prepared by cold pressing and sintering and the other by hot-pressing methods. In addition to differences in fabrication and analysis, the hot-pressed samples had a much larger grain size and contained 0.82 percent iron. The sintered material contained metallic impurities only as spectroscopic traces. The composition of these specimens is given in the following table:

Specimen	Molybdenum (percent)	Silicon (percent)	Oxygen (percent)	Carbon (percent)
Cold-pressed and sintered	62.23	32.70	1.2	0.29
Hot-pressed	62.15	34.79	.42	.34

Resistance values were determined by the following method: Chromel current-carrying electrodes were clamped to the ends of the specimen with leads from a potentiometer attached 1 centimeter inside the current electrodes. A thermocouple was fastened to the center of the specimen and the entire assembly was placed within a bath for the lower temperatures and in a well insulated furnace for the higher temperatures. Resistance of the samples was determined with a Kelvin bridge arrangement.

Bars used for these measurements were:

Large grain, hot-pressed bar; 0.313 by 1.211 centimeters; resistance contacts 6.75 centimeters apart

Cold-pressed and sintered rod; 0.866 centimeter diameter; resistance contacts 6.35 centimeters apart

Modulus of Elasticity

The specimens used for determining the modulus of elasticity were hot-pressed material having the analysis previously given for the electric-resistance samples. A dynamic method similar to that described in reference 4 was employed. With this method, the fundamental frequency of a specimen is determined and the modulus of elasticity is calculated by means of the following equation taken from reference 5:

$$E = 0.96535 \times 10^{-8} \frac{l^3}{h^3} \frac{w}{b} f^2$$

where

E modulus of elasticity (kg/sq mm) (reported values were converted to lb/sq in.)

l length of specimen (cm)

h thickness of specimen (cm)

w weight of specimen (g)

b width of specimen (cm)

f fundamental frequency of resonant vibration of specimen (cps)

Rectangular specimens 0.18 by 0.50 by 3.5 inches in size were used; these specimen were supported by two strings, one from a loudspeaker driving unit, and one from a receiver. The loudspeaker received power from an oscillator through an amplifier and the receiver was connected to an oscilloscope. The fundamental frequency was determined by tuning the oscillator to a resonance peak which was first roughly determined by matching the oscillator signal to the tone obtained by striking the specimen. All determinations were made at room temperature.

RESULTS AND DISCUSSION

Oxidation-Resistance Mechanism

Oxidation of powdered $MoSi_2$. - The ignition temperatures for the small samples rapidly heated in a furnace were 510° and 405° F for 3.0- and 20.0-gram quantities, respectively. A 5-pound quantity of $MoSi_2$ held at 212° F overnight oxidized completely. The residue contained long needlelike crystals of molybdenum trioxide MoO_3 and a white powder considered to be silica.

From this it is apparent that ignition temperature is dependent on the quantity and probably to some extent on the density of the packed specimen. The oxidation reaction is sufficiently exothermic that when the heat produced is retained within a large mass of powder, the resultant temperature of the mass is considerably greater than that of the surrounding atmosphere.

The weight gains of $MoSi_2$ powders standing in still dry air are plotted against time in the oxidation rate curves of figure 3. Appreciable oxidation is evident for the fresh powder; the previously prepared powder, which was considered to have been exposed sufficiently to attain equilibrium at room temperature, is also seen to oxidize at a comparatively rapid rate at 212° F. Evidently, the affinity of $MoSi_2$ powder for oxygen is such as to require a high degree of protection to prevent oxidation. The outstanding oxidation resistance for solid bodies shown in table I would therefore indicate an extremely effective protective coating.

Protective surface coating. - Patterns obtained for both the oxidized and the freshly prepared surfaces of $MoSi_2$ are given in figure 1, which includes a table of d values and a comparison of the relative intensities obtained from both patterns with the A.S.T.M. card data for $MoSi_2$ and α-cristobalite within the angular range covered in this investigation. The d values for the five most important lines of $MoSi_2$ and four important lines of α-cristobalite are in agreement with the card data. In view of differences in techniques used for determining intensities; that is, the powder and photographic method used for the card data and the surface and Geiger counter method used for the specimens, the differences in intensities found were not unexpected. The order of lines of decreasing intensity are in agreement for both substances.

A high-intensity line, not listed in the A.S.T.M. card data, having a d value of 2.04 is found on the unoxidized-surface pattern and is carried through on to the oxidized-surface pattern. Conventional powder patterns of $MoSi_2$ have shown this line; as it is associated with the unoxidized material its presence can hardly affect the identification of the surface coating.

The thinness of the coating is qualitatively indicated by the fact that when the more penetrating copper radiation was substituted for iron the patterns were identical and showed only $MoSi_2$ for both oxidized and unoxidized surfaces.

This evidence of the presence of a silica coating in the form of α-cristobalite, or a siliceous coating containing a large percentage of α-cristobalite, explains the nature of the protective film. Whereas the oxides of both molybdenum and silicon would form on freshly oxidized

surface the molybdic oxide would, at elevated temperatures, be readily volatilized leaving behind a layer of silica possibly combined with some residual molybdenum oxide. This layer could be expected to give protection in oxidizing and neutral atmospheres.

Melting and Casting

Although casting the material at temperatures in the neighborhood of 3800° F was possible, no sound ingots were produced. The use of rammed zirconia molds with the attendant increase in cooling time for the castings seemed to give slightly superior ingots compared with those chill cast in copper but the product was still excessively porous and weak. The porosity was attributed to the decomposition of the $MoSi_2$, an effect further evidenced by the strong evolution of fumes from the melt at and above the melting point. These fumes first became evident just before melting took place and appeared to decrease slightly if the material was held molten 10 or 15 minutes. This phenomenon may indicate that decomposition begins below the melting point and that a more stable composition is approached after the loss of a portion of one of the constituents.

The extent of the decomposition was determined from the analysis of samples taken before and after melting for a charge held fluid at an estimated temperature of 3750° F for 10 minutes.

	Molybdenum (percent)	Silicon (percent)	Oxygen (percent)	Total
Charged to melt	63.78	35.14	0.11	99.03
Ingot	64.78	34.14	----	98.92

The molybdenum increased 1 percent and the silicon decreased the same amount in the ingot. The percentage loss of silicon can be estimated by assuming that no molybdenum was lost and that analysis errors are the same in both determinations. With these assumptions, for a charge of 100 grams, 63.78 grams of molybdenum would pass to the ingot where it could consitute 64.78 percent of the weight of the ingot, which would then weigh $\frac{63.78\ (100)}{64.78} = 98.5$ grams. The ingot contains 34.14 percent silicon or $98.5 \times 34.14 = 33.6$ grams; this amounts to a loss of $35.14 - 33.6 = 1.5$ grams or 4.3 percent of the original silicon. If any molybdenum is lost, the silicon loss is even higher.

The tremendous grain size of the cast material is shown in the photomicrograph presented in figure 4(a). Visual examination of the ingot (fig. 4(b)) reveals considerable porosity.

Experience with the sintering and the hot-pressing processes, in which samples were held at temperatures above 3000° F for prolonged periods of time, has also given rise to the opinion that $MoSi_2$ begins to decompose at some temperature below the melting point but above 3000° F.

Electric Resistivity

Values for the resistivity are plotted against temperature in figure 5. The hot-pressed material, which contains 0.82 percent iron, appreciably less oxygen, and only slightly more carbon than the fine grain material, has a slightly lower resistivity throughout the range investigated. A point of inflection in the two curves, which may be due to a phase change, is apparent but so far uninvestigated. For both materials, the change in resistivity with temperature is linear except in the range from 300° to 600° C as shown by the dashed lines. The temperature coefficient of resistivity has been calculated for the two straight-line portions of both curves using the resistivity at 0° C as a reference.

Specimen	Temperature range (°C)	Temperature coefficient of resistance based on 0° C resistivity (microhm-cm/°C)
Cold-pressed and sintered material	0 to 300	0.00548
	600 to 800	.00756
Hot-pressed material	0 to 300	0.00585
	600 to 1100	.00855

The following three values are given for the electric resistivity of $MoSi_2$ in reference 6:

Temperature (°C)	Electric resistivity (microhm-cm)
-80	18.9
22	21.5
65	22.7

These restivities are lower and a smaller temperature coefficient of resistance is indicated than the values found for the material described herein.

The resistivity of both forms of the $MoSi_2$ is reasonably low as will be seen by comparison with the following data from reference 7:

Material	Temperature (°C)	Electric resistivity (microhm-cm)
$MoSi_2$, hot pressed	20	23.4
Copper, commercial annealed	20	1.724
Mercury	20	95.78
Molybdenum, drawn	20	5.7
Steel, 10 percent nickel 0.1 percent carbon	20	29.0

The relatively low restivity combined with the positive temperature coefficient of restivity indicates that the conductivity of molybdenum disilicide is metallic in nature.

Modulus of Elasticity

Fundamental frequencies and the values of the elastic modulus, as determined by J. H. Kittel, for five specimens were:

Frequency (cps)	Modulus of elasticity (lb/sq in.)
3396	59.1×10^6
2968	58.2
2622	60.2
2869	58.4
2785	58.1
	av. 58.8

The average value for the modulus of elasticity can be compared with values of 28×10^6 to 29×10^6 pounds per square inch for stainless steels and modulus values between 14×10^6 and 18×10^6 pounds per square inch for grey cast iron (reference 8).

The resonance peaks for all specimens were quite narrow, of the order of 3 or 4 cycles in width. This narrowness indicates rather poor damping characteristics for the material at room temperature.

RESULTS AND CONCLUSIONS

The following results were obtained in a study of the oxidation resistance mechanism, the melting characteristics, the electric resistivity, and the modulus of elasticity of molybdenum disilicide:

1. Molybdenum disilicide bodies are protected from oxidation at high temperatures by the formation of a protective siliceous coating in which α-cristobalite has been identified as the sole or principal constitutent.

2. Molybdenum disilicide in powdered form is not inherently resistant to oxidation and burned in air at comparatively low temperatures.

3. Molybdenum disilicide decomposes at the melting point with the loss of appreciable silica. This phenomena has so far prevented casting of satisfactory ingots. Decomposition below the melting point was indicated.

4. The electric resistivity of molybdenum disilicide at room temperature varies from 23 to 27 microhm-centimeters depending on the method of fabrication. The conductivity was found to be metallic in nature and to decrease with increasing temperatures to 2000° F.

5. The room-temperature modulus of elasticity as determined by a dynamic method was 59×10^6 pounds per square inch. Poor damping characteristics are indicated for the material at room temperature.

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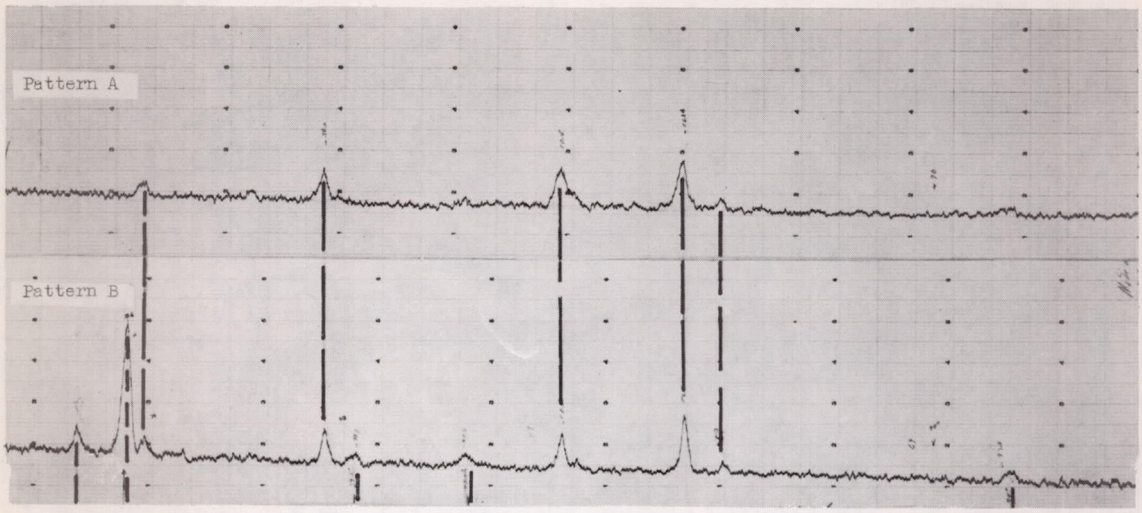
TABLE I - OXIDATION RESISTANCE OF MOLYBDENUM DISILICIDE

WEIGHT CHANGE PER SQUARE CENTIMETER OF SURFACE FOR

EXPOSURE TO AIR AT VARIOUS TEMPERATURES

Temperature (°F)	Exposure (hr)	Unit weight increase (g/(sq cm) (hr))	Reference
2000	75	-0.3×10^{-6}	1
	150	-.4	
2200	200	1.0	2
	300	.7	
2400	50	5.0	1
	100	4.0	
2850	100	-3.67	2
	135	-3.10	



Angle (deg)	Corresponding d value[a] A	Intensity observed I/I_1	A.S.T.M. card data			
			α-cristobalite[b]		Molybdenum disilicide[c]	
			d	I/I_1	d	I/I_1
Pattern A, freshly ground surface etched with hydroflouric acid						
28.5	3.92	38			3.91	40
38.0	2.97	85			2.95	53
50.5	2.26	100			2.25	100
56.8	2.04[d]					
58.8	1.97	31			1.95	27
74.0	1.60	31			1.59	33
Pattern B, surface oxidized 160 hr at 2000° F; lines identical with pattern A omitted						
25.0	4.03					
27.6	4.05	100	4.04	100		
			3.13	16		
39.7	2.85	9	2.85	20		
45.3	2.51	10	2.48	32		
			2.11	5		
			2.02	5		
			1.93	12		
			1.87	12		
			1.69	5		
74.0	1.60	8	1.61	12		
			1.57	1		

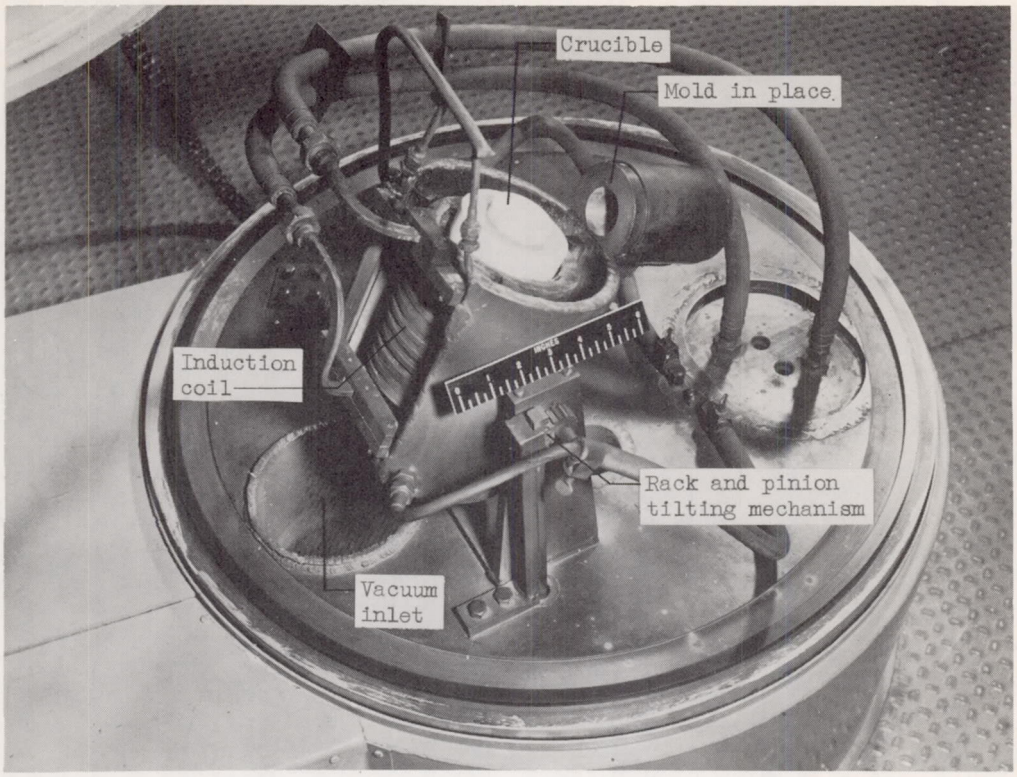
[a]Iron target, manganese filter.

[b]Card 1-0438. High-temperature cubic form for α-cristobalite by Winchell's terminology; I/I_1 by calibrated strips.

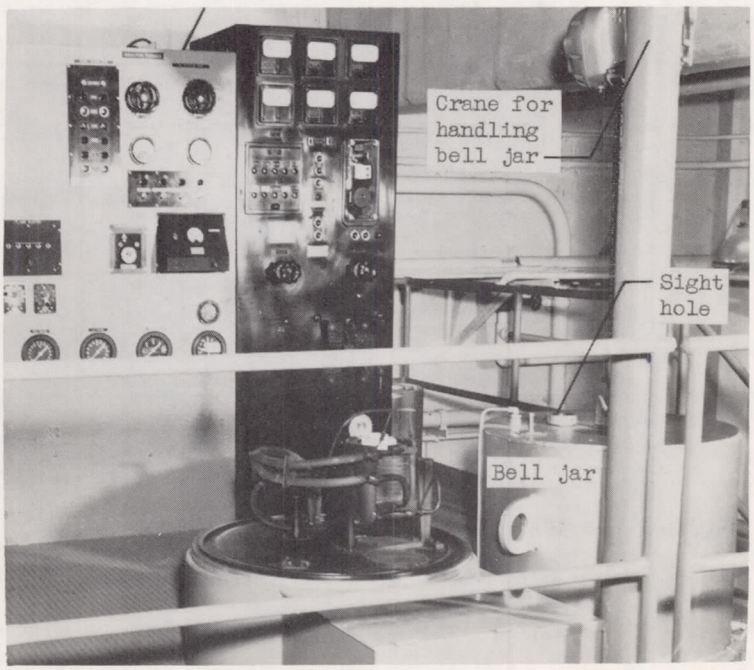
[c]Card 1-1193; I/I_1 by calibrated strips.

[d]Unlisted line of high intensity.

Figure 1. - Patterns and X-ray data for molybdenum disilicide protective coating.

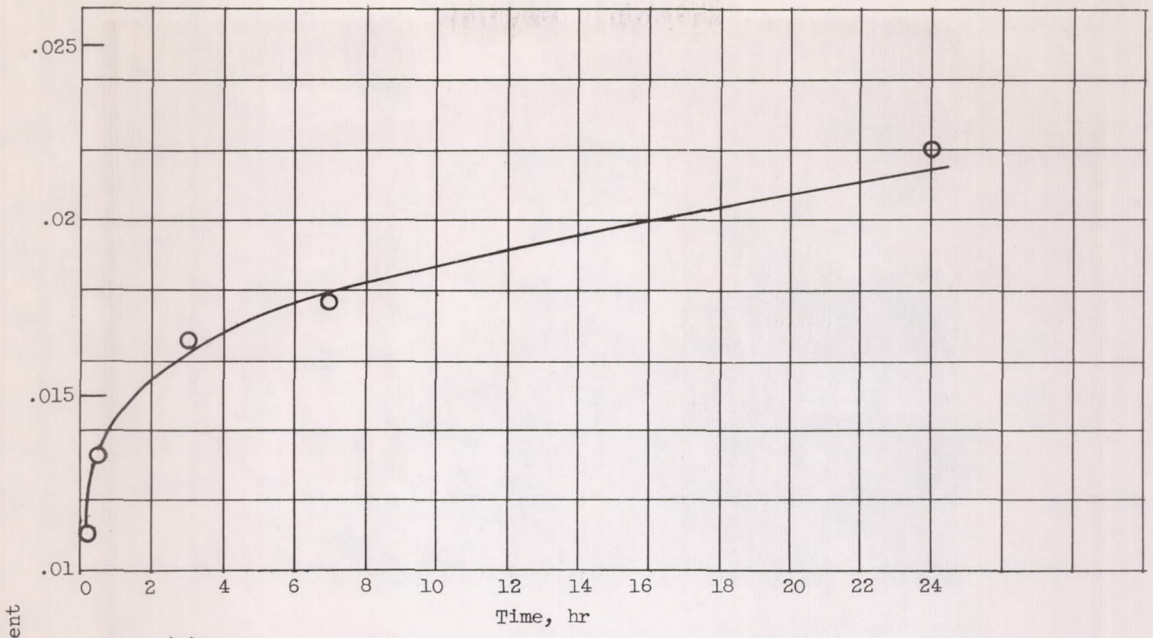


(a) Close-up of crucible and mold unit partly tilted toward pouring position.

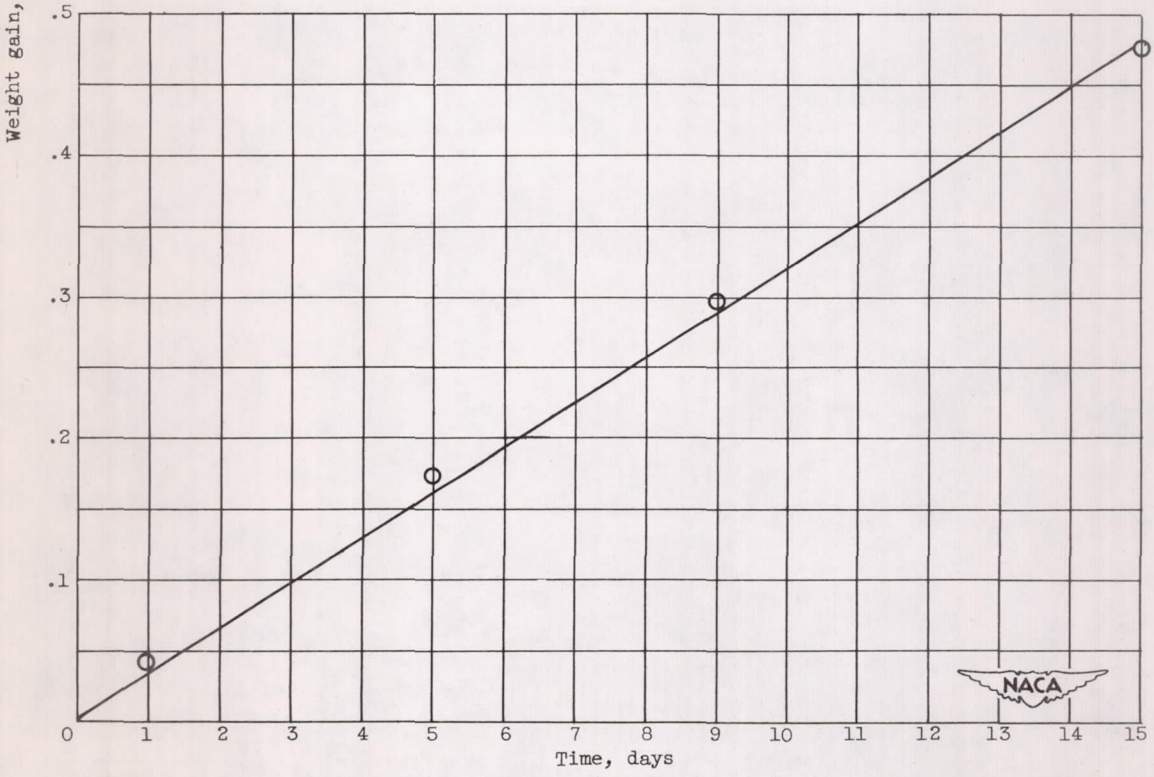


(b) Over-all view showing bell jar removed with control equipment in background.

Figure 2. - Equipment used in melting and casting investigation.

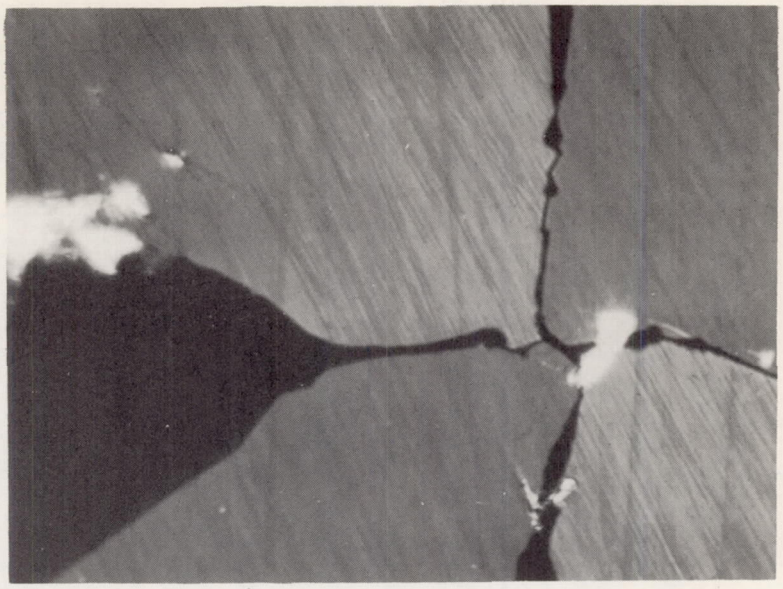


(a) Weight gain of freshly prepared powder at room temperature.

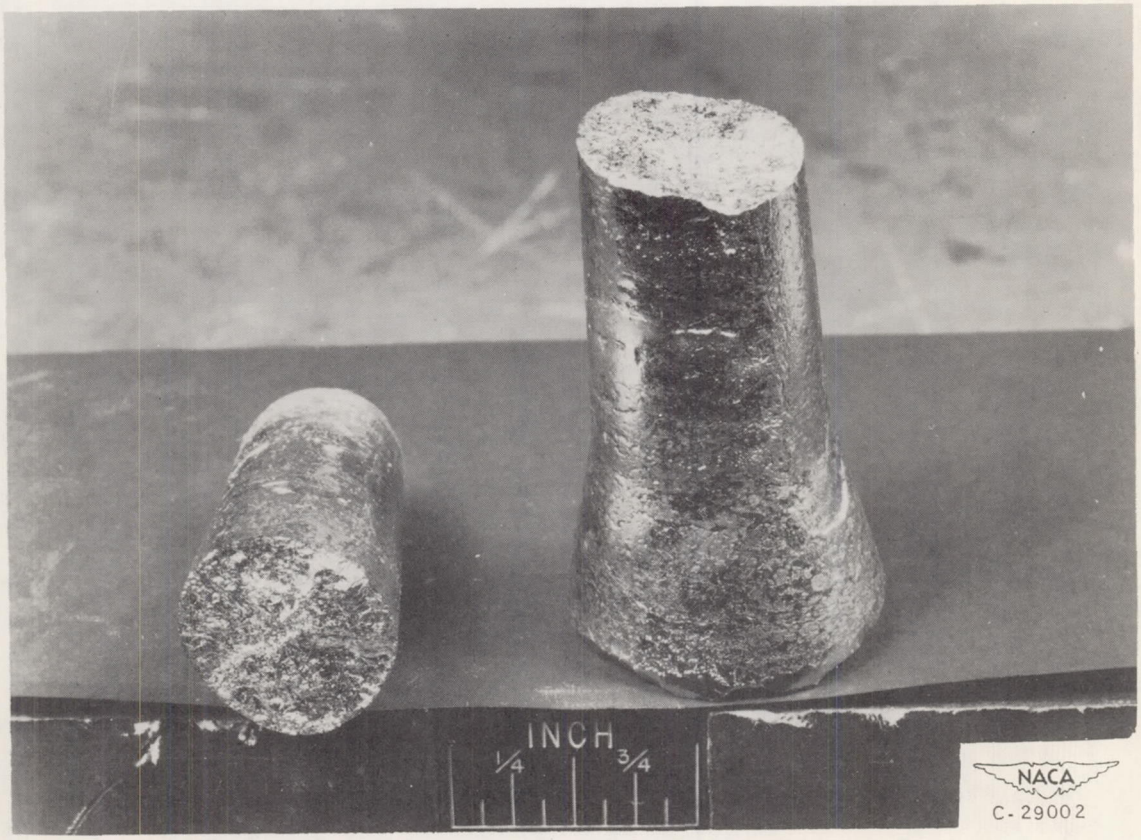


(b) Molybdenum disilicide powder after several weeks of storage. Temperature, 212° F.

Figure 3. - Oxidation characteristic of molybdenum disilicide powder.

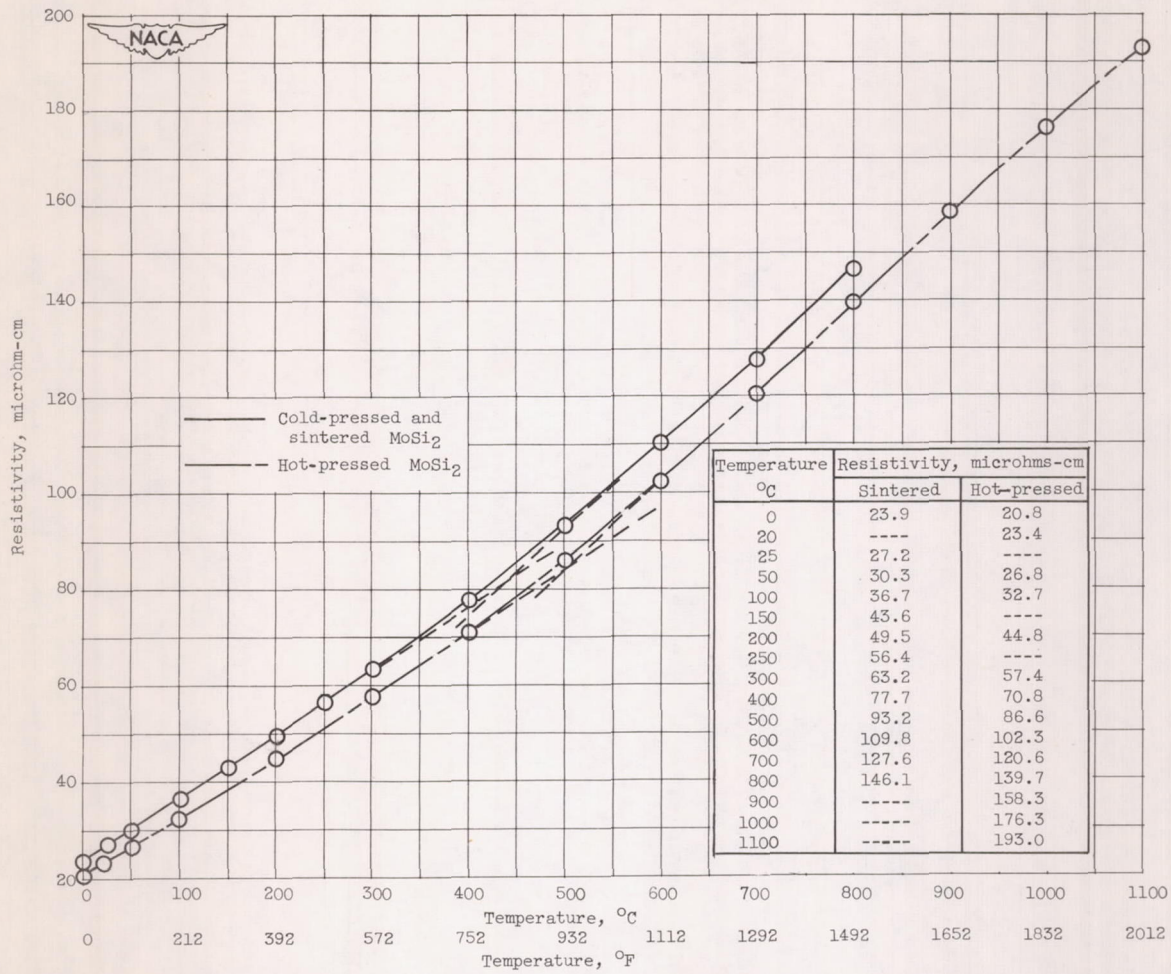


(a) Unetched, cast molybdenum disilicide under polorized light, X1000.



(b) Ingot cast in rammed zirconia mold.

Figure 4. - Cast molybdenum disilicide.



Temperature °C	Resistivity, microhms-cm	
	Sintered	Hot-pressed
0	23.9	20.8
20	----	23.4
25	27.2	----
50	30.3	26.8
100	36.7	32.7
150	43.6	----
200	49.5	44.8
250	56.4	----
300	63.2	57.4
400	77.7	70.8
500	93.2	86.6
600	109.8	102.3
700	127.6	120.6
800	146.1	139.7
900	-----	158.3
1000	-----	176.3
1100	-----	193.0

Figure 5. - Changes in electric resistivity with temperature for two forms of molybdenum disilicide. Cold-pressed and sintered molybdenum disilicide: 1.2 percent oxygen and 0.29 percent carbon. Hot-pressed molybdenum disilicide: 0.42 percent oxygen and 0.39 percent carbon.